



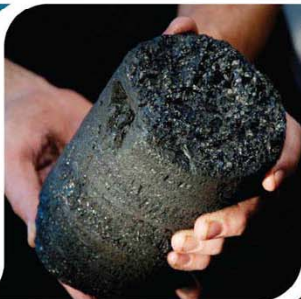
# Understanding MARLAP

## 2011 DoD Environmental Monitoring & Data Quality Workshop

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## DoD QSM Version 4.2

### LOD – Gray Box D-13

For radiological testing, DoD recognizes the terms used in MARLAP to describe the detection capabilities of analytical methods. Specifically, the DL corresponds to the critical value and the LOD corresponds to the minimum detectable concentration or minimum detectable amount. Laboratories performing radiological testing for DoD shall establish and use the minimum detectable concentration according to recommendations contained in MARLAP.



## DoD QSM Version 4.2

### DoD QSM Glossary

**An estimate of the minimum amount of a substance that an analytical process can reliably detect. An LOD is analyte- and matrix-specific and may be laboratory-dependent. .**



# MARLAP

## Critical Value (LOD)

**The MARLAP Glossary defines:**

**Critical Value** as: *In the context of analyte detection, the minimum measured value (e.g., of the instrument signal or the analyte concentration) required to give confidence that a positive (nonzero) amount of analyte is present in the material analyzed. The critical value is sometimes called the critical level or decision level.*

and

**Minimum Detectable Concentration (MDA)** as: *the smallest (true) value of the net state variable that gives a specified probability  $[1 - \alpha]$  that the value of the response variable will exceed its critical value, i.e., that the material analyzed is not blank.*



## DoD QSM Version 4.2

### LOQ – Gray Box D-14

For radiological testing, DoD recognizes the terms used in MARLAP to describe the quantification capabilities of analytical methods. Specifically, the LOQ corresponds to the minimum quantifiable concentration. Laboratories performing radiological testing for DoD shall establish and use the minimum quantifiable concentration according to recommendations contained in MARLAP.



# DoD QSM Version 4.2

## DoD QSM Glossary

**LOQ - The minimum levels, concentrations, or quantities of a target variable (e.g., target analyte) that can be reported with a specified degree of confidence.**





# MARLAP

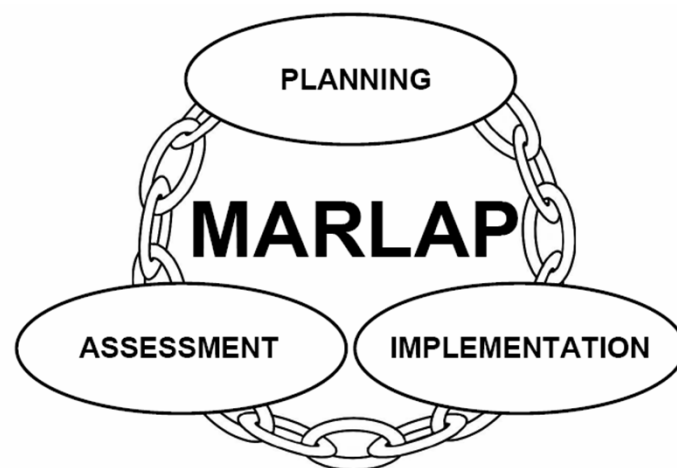
## Minimum Quantifiable Concentration (MQC)(LOQ)

The MARLAP Glossary defines the MQC as:

*Minimum Quantifiable Concentration (MQC) (3.3.7): The minimum quantifiable concentration, or the minimum quantifiable value of the analyte concentration, is defined as the smallest concentration of analyte whose presence in a laboratory sample ensures the relative standard deviation of the measurement does not exceed a specified value, usually 10 percent.*



# Multi-Agency Radiological Laboratory Analytical Protocols



July 2004



## In General MARLAP recommends:

- Use a performance-based approach where possible
- Use validated approaches to measurements
- Use measurement uncertainty as basis for decisionmaking
- Ensure that data quality is sufficient for decisionmaking by linking QC to MQOs



## UFP QAPP

- A QAPP presents the steps that should be taken to ensure that environmental data collected are of the correct type and quality required for a specific decision or use.
- Definitive data — Analytical data of known quality, concentration, and level of uncertainty.



## Where to Now?

- We will talk about several principles recommended by MARLAP pertaining to uncertainty and detection capability
  - MARLAP approach to detection and uncertainty
  - Statistics again
  - Sources of uncertainty
  - Type B vs. Type A evaluations of uncertainty
  - How does quality control relate to uncertainty and detection statistics?
  - Conclusions, Issues of Concern, and Future Work

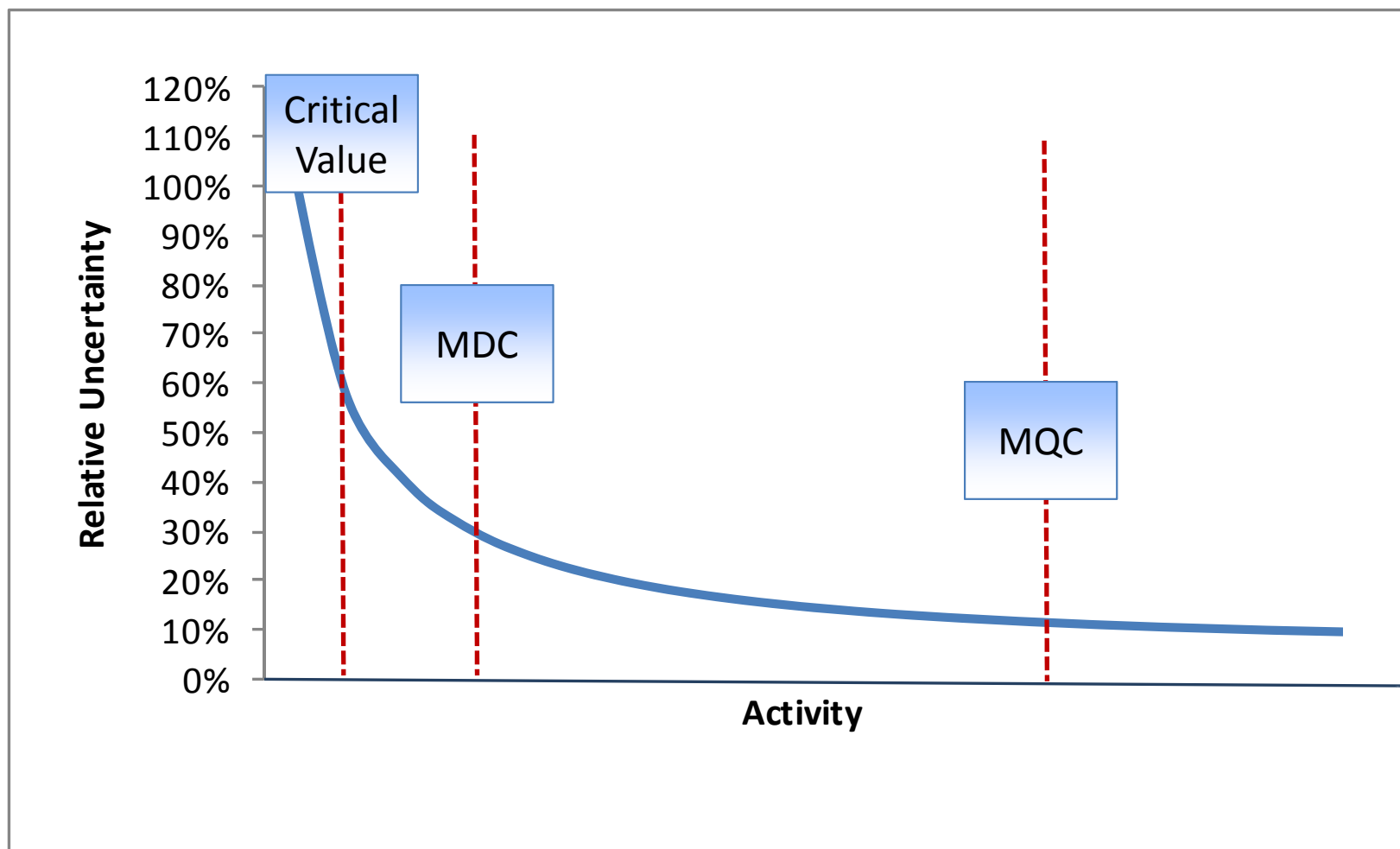


# MARLAP Approach to Detection

## MARLAP 20.2.5

- Detection in radiochemistry based on the uncertainty of the instrument signal obtained by counting analyte-free sources;
- Should be based on the uncertainty obtained when analyte-free samples are analyzed.

## Critical Value, MDC and MQC





## MARLAP Recommendations on Uncertainty MARLAP 19.3.9

- Adopt terminology and methods of the GUM for evaluating and reporting uncertainty.
- Account for both random and systematic effects
- Do not account for blunders or spurious errors.
- Consider all possible sources of measurement uncertainty





## MARLAP Recommendations on Uncertainty MARLAP 19.3.9

- Evaluate and propagate uncertainty from all sources believed to be potentially significant in the final result.
- Follow QC procedures that ensure a state of statistical control, which is a prerequisite for uncertainty evaluation.

# GUM

## Law of Propagation of Uncertainty

$$\text{for : } y = \frac{f(x_1 x_2 \dots x_n)}{z_1^2 z_2^2 \dots z_m^2}$$

$$u_c^2(y) = \sum_{i=1}^N \left( \frac{\partial f}{\partial x_i} \right)^2 u_c^2(x_i) + 2 \sum_{i=1}^{N-1} \sum_{j=i+1}^N \frac{\partial f}{\partial x_i} \frac{\partial f}{\partial x_j} u_c^2(x_i, x_j)$$

$$u_c^2(y) = \sum_{i=1}^N \left( \frac{\partial f}{\partial x_i} \right)^2 u_c^2(x_i)$$

## Special Form of the Uncertainty Propagation Formula (MARLAP 19.4.3.3)

$$u_c(y) = \sqrt{\frac{u_c^2(f(x_1 x_2 \dots x_n))}{z_1^2 z_2^2 \dots z_m^2} + y^2 \left( \frac{u^2(z_1)}{z_1^2} + \frac{u^2(z_2)}{z_2^2} + \dots + \frac{u^2(z_m)}{z_m^2} \right)}$$

so for :  $AC = \frac{R_s/t_s - R_b/t_b}{\varepsilon V}$

$$u_c^2(AC) = \sqrt{\frac{R_s/t_s + R_b/t_b}{\varepsilon^2 V^2} + AC^2 \left( \frac{u^2(\varepsilon)}{\varepsilon^2} + \frac{u^2(V)}{V^2} \right)}$$

# Sources of Uncertainty



- Reasonable estimates of uncertainty include all factors that contribute uncertainty.
- Not all sources of uncertainty may be significant but they should at least be considered:
  - radiation counting
  - instrument calibration (e.g., counting efficiency)
  - tracers, carriers
  - contamination of reagents and tracers
  - yield measurement
  - instrument backgrounds
  - crosstalk and spillover



## GUM Type B Evaluation of Uncertainty

- Type B estimations are based on experience, knowledge of process – not on measurements
  - Different distributions–trapezoidal, rectangular, others
  - Imported values (e.g., branching ratios)
  - Radiation counting – Poisson Uncertainty (a.k.a. count uncertainty)
- May be limited or inappropriate due to an incomplete or faulty understanding of the process



## GUM Type B Evaluation of Uncertainty Radiation Counting

- Square root of the counts as an estimate of Poisson uncertainty of a count
  - A significant and variable component of uncertainty
  - Represents the minimum uncertainty due to the random nature of radioactivity counting
  - Not always sufficient since non-Poisson sources contribute to uncertainty



# MARLAP Warns...

## Section 19.5.5

- It is inappropriate to use the Poisson model:
  - *If the amount of blank contaminant varies between measurements*
  - *If the causes of blank contamination are simply not well understood.*
- *It is usually necessary to determine the blank level and its uncertainty by replicate measurements (a Type A evaluation).*



# GUM Type A Evaluation of Uncertainty

MARLAP 19.4.2.1

- **Determined by a series of experimental observations**
  - Activity of blanks or background
  - Activity of spiked samples
- **Also:**
  - Volume measurements (e.g., pipetting)
  - Mass (i.e., weighing)
  - Tracer or carrier concentration
  - Etc., etc.



# GUM Type A Evaluation of Uncertainty

## MARLAP 19.4.2.1

We calculate the mean and standard uncertainty and use these as an input for uncertainty propagation

$$\bar{X}_i = \frac{1}{n} \sum_{k=1}^n X_{i,k} \quad s^2(X_{i,k}) = \frac{1}{n-1} \sum_{k=1}^n (X_{i,k} - \bar{X}_i)^2 \quad s(\bar{X}_i) = \frac{s(X_{i,k})}{\sqrt{n}}$$

$$u(x_i) = \sqrt{\frac{1}{n(n-1)} \sum_{k=1}^n (X_{i,k} - \bar{X}_i)^2}$$



# Batch QC Samples, Uncertainty & Detection Statistics

- Batch QC Samples are all observed measures of method performance
  - Blanks (No activity on average)
  - LCS (No bias on average)
  - Duplicates (Agree within calculated uncertainty)



# Testing Method Blanks for Absolute Bias

## MARLAP 6.4.4.1 and 6A.2

Important when one of the purposes is to determine whether analyte is present in a sample or a sampled population

$$|T| = \frac{|\bar{X}|}{\sqrt{s_x^2 / \sqrt{N}}}$$

$$v_{\text{eff}} = (N-1) \left( 1 + \frac{u^2(K)}{s_x^2 / N} \right)^2 \quad |T| > t_{1-\alpha/2}(v_{\text{eff}})$$

**PG**

## Calculating Excess Variance from Blanks

$$u_c^2(x_{blanks}) = u^2(x_{1fromPoisson}) + u^2(x_{1excess})$$

$$u(x_{1excess}) = \sqrt{u_c^2(x_{blanks}) - u^2(x_{1fromPoisson})}$$

## Estimating Critical Value Using Blanks

### MARLAP

$$\hat{B} = F(Z_B) \quad (20.12)$$

where

$F$  is the calibration function for the laboratory sample measurement, whose parameters include the instrument background, counting efficiency, chemical yield, and any estimated interferences and

$Z_B$  is the estimated absolute activity of the blank.

Then the net count is  $\hat{S} = \hat{Y} - \hat{B}$ , whose critical value is

$$S_C = z_{1-\alpha} \sqrt{\sigma^2(\hat{Y}_0) + \sigma^2(\hat{B})} \quad (20.13)$$

where

$\sigma^2(\hat{Y}_0)$  is the variance of the gross count  $\hat{Y}$  in the test source measurement when the sample is analyte-free and

$\sigma^2(\hat{B})$  is the variance of the estimator  $\hat{B}$ .

If Poisson counting statistics are assumed, then  $\sigma^2(\hat{Y}_0)$  may be estimated by  $\hat{B}$  (assuming  $\hat{B} > 0$ ), but estimating  $\sigma^2(\hat{B})$  still requires a more complicated expression, which may be based on uncer-



# Conclusions, Potential Issues for Consideration, and Future Work

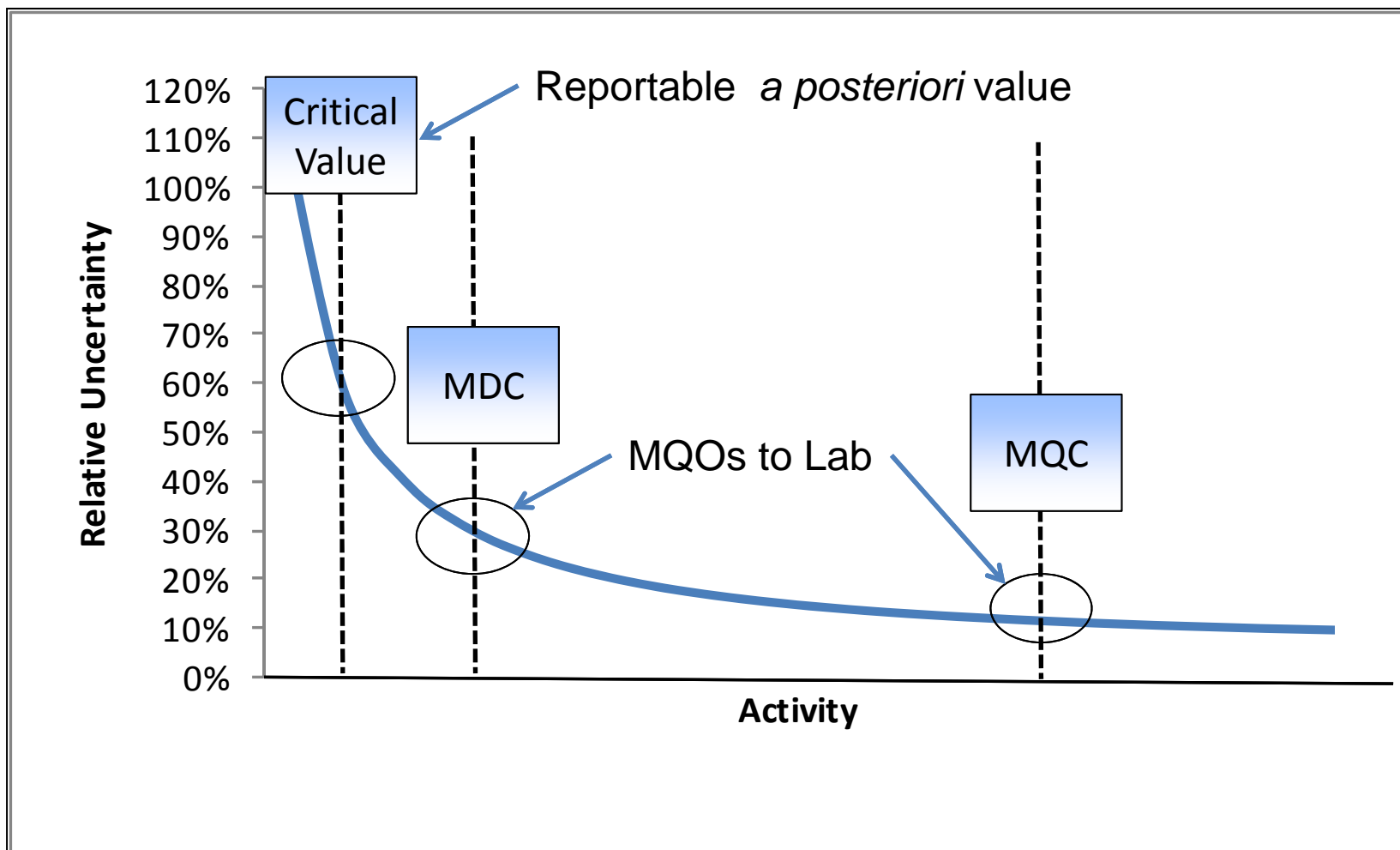
- Following the QSM requirements requires evaluation of uncertainty per GUM
- Blank samples can be used to test the process for absolute bias.
- Other QC samples can be used to test for relative bias
- Uncertainty and Detection must be assessed across the entire range

# Conclusions, Potential Issues for Consideration, and Future Work



- Type A estimates of uncertainty (without checking) may lead to low estimates of uncertainty in the background
- Estimating the uncertainty at the MDC may require samples spiked at the level of the MDC
- Future work will present more detailed application of the approach to estimating

## Critical Value, MDC and MQC





# MARLAP



## NUREG-1576, Vol 2, Part III

**Chap 18 LABORATORY QUALITY CONTROL**

**Chap 19 MEASUREMENT UNCERTAINTY**

**Chap 20 DETECTION AND QUANTIFICATION  
CAPABILITIES**

# MARLAP



<http://www.nrc.gov/reading-rm.html>

<http://www.epa.gov/radiation/marlap/>

**NUREG-1576, Vol 1, " Multi-Agency Radiological Laboratory Analytical Protocols Manual (MARLAP)," Part I: Chapters 1-9 Appendices A - E (Volume I).**

**(Primarily for project planners - DQOs and MQOs)**

**NUREG-1576, Vol 2, " Multi-Agency Radiological Laboratory Analytical Protocols Manual (MARLAP)," Part II: Chapters 10-17 - Appendix F. and Part III: Chapters 18-20 – Appendix G**

**(Technical guidance for radiochemists, auditors, project planners)**

**NUREG-1576, Supp 1, " Multi-Agency Radiological Laboratory Analytical Protocols Manual (MARLAP)," Accompaniment to CD - Executive Summary (Roadmap)"**



# Other Key Documents

- **GUM**

- Evaluation of measurement data — Guide to the expression of uncertainty in measurement; JCGM 100:2008 GUM 1995 with minor corrections <http://www.bipm.org/en/publications/guides/gum.html>

- **ANSI N42.23**

American National Standards Institute (ANSI). 2004a. *American National Standard Measurement and Associated Instrument Quality Assurance for Radioassay Laboratories*. The Institute of Electrical and Electronics Engineers, Inc. ANSI N42.23-1986 (R2004). Available from: <http://www.ansi.org/>.

- **IUPAC**

- J. Inczédy, T. Lengyel, A.M. Ure, International Union of Pure and Applied Chemistry, *Compendium of Analytical Nomenclature, Definitive Rules 1997*, 3rd Edition, Blackwell Science (1998).



# Thank You Very Much

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